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COMPLETE SPECIFICATION

A process for the catalytic hydrogenation of carbon monoxide

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FÜR BERGBAU UND CHEMIE, a German Company of (22A) Homberg, Niederrhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for carrying out the hydrogenation of carbon monoxide in the presence of a hydrogenation catalyst of the 8th group of the periodic system at elevated temperatures and, if necessary, under high pressure.

The hydrogenation of carbon monoxide by means of elementary hydrogen in the presence of a hydrogenation catalyst of the 8th group of the periodic system is well known in the art. Recently, it has also been proposed to add to the mixture of carbon monoxide and hydrogen reactive substances, such as olefins, alcohols, aldehydes, ketones and acids, which reactive substances are then built up, during the synthesis, into products of higher molecular weight. It is also known to increase or reduce the number of carbon atoms in the molecules of hydrocarbons when the hydrogenation of the carbon monoxide is carried out with elementary hydrogen in the presence of the hydrocarbons. All of these syntheses consist in the hydrogenation of carbon monoxide with elementary hydrogen with the addition of reactive organic compounds, the carbon monoxide hydrogen ratio in the initial synthesis gas varying within wide limits in accordance with the operating conditions, with the type of catalyst used and with the products desired.

In all of these processes it is necessary to use effective catalysts in order to obtain a sufficiently strong activation of the hydrogen as well as an activation of the carbon monoxide, and it is essential for the activation of these two starting materials to be so adjusted to each other that the synthesis does not result solely in the formation of methane as may, for example, occur with excessive activation of the hydrogen, and that an excessive separation of carbon, as occurs with excessive activation of the carbon monoxide, is avoided.

It is also known to react acetylene, olefins, and substances with mobile or reactive hydrogen atoms, with carbon monoxide. These reactions, however, only occur in the presence of metal carbonyls and metal carbonyl hydrides.

Furthermore, it is known to react water gas and steam with olefinic compounds in the presence of catalysts at elevated temperature and under elevated pressure, whereby oxygen-containing organic compounds are obtained.

It has also been proposed to react olefinic compounds with carbon monoxide and water at elevated temperature and under elevated pressure in the presence of carbonyl-forming metals and/or of compounds of carbonyl-forming metals and hydrogenation catalysts, whereby oxygen-containing compounds, particularly aldehydes or ketones, are obtained.

According to the invention, it has now been found that the elementary hydrogen required for the hydrogenation of the carbon monoxide in the presence of a hydrogenation catalyst of the 8th group of the periodic system and with the use of an aliphatic compound which contains no unsaturated carbon-carbon bonds and which is reactive under the process conditions, may be replaced in whole or in part by steam. The surprising feature is that steam is known to exert an extremely deleterious effect on the catalysts used in the hydrogenation of carbon monoxide, because the structure of the catalysts is changed, for

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example, by oxidation. The invention constitutes a substantial advance in the art inasmuch as it is now no longer necessary to produce carbon monoxide-hydrogen mixtures in a complicated manner, or to produce the hydrogen by reacting the carbon monoxide with steam, it being now sufficient to have carbon monoxide, or gases which contain carbon monoxide, react together with steam on the saturated aliphatic compounds, such as alcohols, aldehydes, ketones, hydrocarbons and amines. The economic advantage achieved by this advance in the art is obvious, for it is known that it is far simpler and cheaper to produce carbon monoxide, or gases containing carbon monoxide, such as generator gas and blast-furnace gas, than to prepare mixtures of carbon monoxide and hydrogen. It has also been found that in many cases the reduction of carbon monoxide proceeds much more readily by means of the process of the invention than when elementary hydrogen is used, so that the processing of gases poor in carbon monoxide is particularly facilitated.

When the catalyst is used in the form of metal, or in quasi-metallic form, such as a carbide or nitride, the partial pressure of steam in the carbon monoxide/steam mixture should not exceed one-half of the total pressure of that gas mixture. The process according to the invention can also be carried out in such manner that for the hydrogenation of the carbon monoxide only part of the hydrogen hitherto used is replaced by steam.

When the aliphatic compound employed in the process according to the invention is a saturated hydrocarbon, this is converted into one or more hydrocarbons of higher molecular weight or is degraded to one or more compounds of lower molecular weight.

The invention is illustrated by the following examples:—

EXAMPLE 1

This example illustrates the process of the invention carried out with the use of an alcohol as the aliphatic compound.

A cobalt catalyst known in the OXO synthesis and consisting of cobalt, THO_2, copper and kieselguhr in the proportion 100: 18: 3: 100 was first reduced with electrolytic hydrogen for 4 hours at 400°C. and at a space velocity of 500. 1 mol of methanol vapour was then added to a carbon monoxide/steam mixture containing 1 mol of steam per 3 mols of carbon monoxide, this gas-vapour mixture being passed over the cobalt catalyst at a gauge pressure of 100 atmospheres and at a temperature of 210°C. Approximately 30% of the methanol was converted during the reaction. With a CO-conversion of 90%, the converted methanol appeared in the synthesis product substantially in the form of ethyl alcohol, together with small quantities of methyl acetate and ethyl acetate.

EXAMPLE 2

This example illustrates the synthesis of hydrocarbons from a saturated aliphatic hydrocarbon of lower colecular weight.

A carrier-free iron catalyst composed of 100 parts of Fe, 0.25 parts of Cu, 0.5 parts of K_2CO_3 was precipitated from a nitrate solution in known manner by means of a solution of sodium carbonate, the precipitate being impregnated with K_2CO_3. From the dried catalyst thus obtained, a catalyst suspension was prepared, the suspension medium being a paraffinic hydrocarbon oil boiling in the range 350°-450°C. the concentration of the suspension being such that it contained 10% of Fe.

For reduction of the catalyst, CO was passed through the suspension at 270°C and at a gauge pressure of 3 atmospheres for a period of 20 hours at the rate of 1 normal litre of CO per gram of Fe per hour.

After reduction, the catalyst was operated in the liquid phase at 260°C. and at a gauge pressure of 20 atmospheres with a carbon monoxide/steam mixture containing 3 mols of carbon monoxide per mol of steam, to which was added 10% by volume of methane based on the carbon monoxide. The gas throughout was 1.6 normal litres of carbon monoxide per gram of Fe per hour.

Under these conditions and with a CO-conversion of 92%, approximately 40% of the methane employed took part in the reaction. Of the methane converted, approximately 60% was upgraded to ethane, 30% to propane and the remainder to a mixture of ethylene, propylene, butylene and butane.

EXAMPLE 3

This example illustrates the degradation of a saturated aliphatic hydrocarbon to hydrocarbons of lower molecular weight.

A supported iron catalyst having the following composition:—100 parts of Fe, 10 parts of Mg, 10 parts of Cu, 50 parts of kieselguhr, and 0.5 parts of K_2CO_3, was precipitated from a nitrate solution in known manner by means of a hot sodium carbonate solution followed by impregnation with K_2CO_3, and reduced for a period of 48 hours at normal pressure and at 230°C. by means of a hydrocarbon synthesis gas of the composition $CO:H_2=1:2$. When a carbon monoxide/steam mixture containing 3 mols of CO per mol of H_2O was passed over this reduced catalyst at a gauge pressure of 20 atmospheres and at a temperature of 270°C., and at a gas space velocity of 100 litres of CO per litre of catalyst per hour, there were obtained, with a CO-conversion of 92% per normal cubic metre of CO used; 170 grams of products having the following composition:—

12 grams of methane
5 ,, ,, ethane
10 ,, ,, ethylene
51 ,, ,, propylene and butylene ("gasol")
92 ,, ,, C_5 and higher hydrocarbons, including 6.5 grams of pentane

When, under otherwise similar conditions, pentane in an amount of 2.5% by volume based on the CO used, was added to the carbon monoxide/steam mixture, there were obtained, with an equal CO conversion per normal cubic metre of CO used, 248 grams of products having the following composition:—

34 grams of methane
19 ,, ,, ethane
18 ,, ,, ethylene
62 ,, ,, propylene and butylene ("gasol")
115 ,, ,, C_5 and higher hydrocarbons, including 26.5 grams of pentane

Therefore, statistically, 64% of the pentane used were degraded to lower hydrocarbons, predominantly to CH_4.

EXAMPLE 4

This example illustrates the synthesis with the incorporation of an amine in the carbon monoxide/steam mixture.

Electrolytic hydrogen was first passed for three hours at a space velocity of 1000 litres of H_2 per litre of catalyst per hour over a carrier-free Fe/Cu catalyst (100 parts of Fe, 10 parts of Cu, 0.5 parts of K_2CO_3), which has been prepared in known manner by precipitation from a nitrate solution by means of sodium carbonate and subsequent impregnation of the precipitate with K_2CO_3. The catalyst was then treated for three hours with ammonia at 300°C. and at a space velocity of 1000. In this manner a catalyst was obtained 50% of which consisted of a nitride of the statistical formula $Fe_{1.3}N$. When a carbon monoxide/steam mixture containing 3 volumes of CO per 1.2 volumes of steam was passed, at a gauge pressure of 10 atmospheres, at a temperature of 240°C. and at a space velocity of 100 based on the CO used, over this nitride catalyst, in admixture with methylamine in an amount of 10% by volume based on the CO used, there was obtained, with a CO conversion of 93%, 239 grams of a reaction product per normal cubic metre of CO used. This reaction product contained:—

12 grams of C_1+C_2 hydrocarbons
116 ,, ,, C_3 and higher hydrocarbons
61 ,, ,, secondary dimethylamine
36 ,, ,, tertiary trimethylamine; and
11 ,, ,, a mixture of higher primary, secondary, and tertiary amines.

EXAMPLE 5

This example illustrates the synthesis with the use of an aldehyde with carbon monoxide/steam mixture.

A cobalt catalyst of the composition 100 parts of cobalt, 15 parts of thorium, 3 parts of magnesium, and 200 parts of kieselguhr, was reduced with electrolytic hydrogen at 450°C. under normal pressure and at a gas space velocity of 500 for a period of five hours. When a carbon monoxide/steam mixture containing 3 volumes of CO:1.25 volumes of steam and with which 1 volume of acetaldehyde was admixed, was passed over the reduced catalyst at 200°C. and under a gauge pressure of 110 atmospheres, 65% of the acetaldehyde took part in the reaction. With a CO conversion of 90%, 30% of the converted acetaldehyde appeared as ethyl alcohol, 34% as propionaldehyde, 8% as isopropyl alcohol, and 19% as ethyl acetate with small amounts of a mixture of aldehydes, alcohols, acids and esters of higher molecular weight.

EXAMPLE 6

This example illustrates the use of a ketone with the carbon monoxide/steam mixture.

When under otherwise similar conditions as those used in Example 5, 1 volume of acetone was admixed with the carbon monoxide/steam mixture (1 volume of acetone per 3 volumes of CO), 30% of the acetone took part in the reaction. With a CO conversion of 91%, 48% of the converted acetone was present in the reaction products as secondary propyl alcohol, 21% as butanone (methyl ethyl ketone), 15% as secondary butyl alcohol, 11% as propyl acetate and 5% in the form of a mixture of higher alcohols, ketones, acids and esters together with hydrocarbons.

What we claim is:—

1. In a process for the hydrogenation of carbon monoxide carried out in the presence of a hydrogenation catalyst of the 8th group of the periodic system at elevated temperature and with the addition of an aliphatic compound which contains no unsaturated carbon-to-carbon bond and which is reactive under the process conditions, the step which comprises effecting the hydrogenation with a mixture of hydrogen and steam.

2. In a process for the hydrogenation of carbon monoxide carried out in the presence of a hydrogenation catalyst of the 8th group of the periodic system at elevated

temperature and with the addition of an aliphatic compound which contains no unsaturated carbon-to-carbon bond and which is reactive under the process conditions, the step which comprises effecting the hydrogenation wholly with steam.

3. A process according to Claim 1 or Claim 2, in which the partial pressure of the steam in the carbon monoxide/steam mixture used does not exceed one-half of the pressure of that gas mixture when the catalyst is used in the form of metal, carbide, or nitride.

4. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to any one of the Examples.

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